Boardman (W. E.)

[*From the Fifth Annual Report of the State Board of Health.*]

ON THE USE

OF

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ZINCED OR GALVANIZED IRON

FOR

THE STORAGE AND CONVEYANCE OF DRINKING-WATER.

By W. E. BOARDMAN, M.D., of Boston.

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BOSTON:
WRIGHT & POTTER, STATE PRINTERS,
79 Milk Street, Corner of Federal.
1874.

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USE OF ZINCED OR GALVANIZED IRON.

The Report of the State Board of Health of Massachusetts, for the year 1871, contains a paper upon "Poisoning by Lead-Pipe," which is confirmatory of the now well-recognized fact, as illustrated in the following paragraph (p. 40):—"From the evidence presented in the preceding pages, it seems reasonable to believe that the use of lead-pipe for the conveyance of drinking-water is always attended with a certain degree of danger, because such water always contains lead; and that this danger varies in degree with the character of the water conveyed and the susceptibility to lead poison of those who drink it."

With the view of obviating the dangers arising from the use of lead-pipe, different methods and materials have been suggested from time to time. In this way, zinced (or what is termed commonly galvanized) iron has come into use, and at the present time is extensively employed, both in this country and in Europe, for the purpose of roofing material, gutters and conductors, reservoirs, water-conduits, bathing-tubs, cooking utensils, etc.

The object of the present paper is to determine, if possible, whether or not the employment of this material for the storage and conduction of drinking-water is attended with danger of zinc poisoning, as has been re-affirmed recently.*

The various modes of protecting iron, *with the exception of mere superficial coverings*, have all been of the electro-chemical class, and have been derived, in various ways, from suggestions deduced from the experiments and observations of Sir Humphry Davy,† for the protection of the copper sheathing

* Boston Journal of Chemistry, Vol. V., 1871, *passim*.

† Phil. Trans., Vol. CXIV., 1824, and Phil. Mag., 1st Ser. Vols. LXIV. and LXV.

of vessels. In his paper on this subject, the author developed the principle of counteracting chemical by electrical forces. Subsequently his idea was adapted to particular cases. He stated that it follows from the principles which he developed, that cast or wrought iron may be preserved from chemical action by suitable protectors of zinc or tin. Prof. Edmund Davy was the first to publish * a series of experiments which he undertook with the view of determining this protective power of zinc, which he employed in simple contact and in massive form. Shortly after the publication of the results of these experiments by Prof. Davy, M. Sorel, a French engineer, obtained a patent for the protection of iron against rust by coating its surface with fluid zinc, and, with this patent, the first manufactories of zinced or galvanized iron were established in London, under the style of the "British Galvanization of Metals Company," and the "Zinced or Galvanized Iron Company." Prof. E. Davy, however, claiming priority of discovery, stated that he had employed this method of zincing iron so far back as 1834, yet we have no other record of such experience than his simple statement. Without knowledge of the principle, however, Madame Leroi de Jancourt was granted a patent on the 26th of September, 1791, for preserving metals from rust by covering them with an alloy of zinc, bismuth and tin.

Zinced or galvanized iron is prepared by dipping the iron, previously well cleaned by means of dilute acid, into melted zinc. By this process, the iron becomes superficially combined with the zinc, and there is furnished, as claimed by the first manufacturers, a material which is adapted for use as water-pipes, reservoirs, etc., is durable, cheap, and is unattended with danger to the human system in the way that lead is when employed for similar purposes.

In order to discuss connectedly and to the best advantage the subject which we have in view, it has been deemed advisable to consider it under the following heads, viz. :—

1. Is the zinc of galvanized iron acted upon by water, and what are the products of such action?

* Report of the British Association for 1835.

2. Do these products exert a poisonous action upon the human system?

1. The action of water upon zinc has been recognized for a long time. In the year 1778, M. de la Falie, a French physician and chemist, in place of vessels of iron, copper, etc., then employed for culinary purposes, proposed the use of iron vessels lined with zinc, principally upon three grounds; namely, because, in his opinion, the zinc would not be dangerous; such vessels would not be very expensive, and they would be more durable.* A subsequent report to the French Academy of Sciences disapproved of the use of these vessels, on the ground that the zinc is removed and endangers the health. Discoveries of new sources of supply of the metal and of the means of rendering it more useful in the arts, led to the revival of its employment, by MM. Douey and Montagnac, in the manufacture of culinary articles, roofing materials, reservoirs, water-conduits, etc. The first petitions of these gentlemen to the proper authorities having been reported upon unfavorably, by MM. Thenard and Gay-Lussac,† they made another petition which led to a series of experiments by MM. Vauquelin and Deyeux,‡ under the authority of the Academy of Sciences. In their report they state that zinc is acted upon by water, the weakest vegetable acids and butter; that water, allowed to stand in zinc vessels, was partly decomposed and a white oxide was produced, while the water covering the oxide had a metallic taste.

M. Schaufèle § made a series of careful experiments, the results of which were confirmed later by distinguished chemists, notably by Payen and Chevallier,‖ with the view of determining the action of various substances upon zinc. He found that common water, allowed to stand in a galvanized iron vessel, presented traces, very slight indeed, of zinc at the expiration of thirteen hours; that common water, placed in pure zinc vessels, gave no indication of the presence of

* Annales de Chimie, t. 86, p. 51. 1813.

† Jour. de Méd. de Corvisart, t. 36, p. 225.

‡ Annales de Chimie, t. 86, p. 51. 1813.

§ Jour. de Chim. Méd., t. iv., p. 663, 1848, and Tardieu, Dict. d'Hyg. Publique, t. 3, p. 708. 1854.

‖ Tardieu, loc. cit.

zinc; that distilled water showed traces of zinc, in five hours, both in pure zinc and galvanized iron vessels.

Similar results have been reported by numerous reliable observers. Prof. Wm. Ripley Nichols, of the Massachusetts Institute of Technology, remarked to the writer that he always expects to find zinc in water which passes through galvanized iron pipes, and, in a written communication, he stated that a specimen of water drawn from the pipes, which have been in use in the Institute for eight or nine years, contained a small amount of zinc in suspension, and in solution an amount equal to 0.062 grain to the gallon. The water had remained undisturbed in the pipes for about thirty-six hours.

Another specimen of water was examined by Prof. Nichols, at the request of the writer. It was spring-water which had passed through between forty and fifty feet of zinced pipe, from which no water was drawn previously for about twenty-four hours. The analysis gave rise to a suspicion of drainage contamination, and detected a trace of zinc in suspension and 0.843 grain to the gallon in solution.

This subject of the action of water on zinc has been most ably treated by Robert Mallet,* who drew up a series of papers showing the results of experiments made by himself, with the view of determining the best protector for iron against corrosion by air and water. Among the conclusions derived from his prolonged and carefully conducted experiments, the following may be quoted in proof of the affirmative of our question:—

"Of Cast-iron in Simple Contact with Zinc, Immersed in Fresh Water.

"If cast-iron be perfectly free from any initial stains of rust and quite homogeneous in texture, it is electro-chemically preserved by an equal surface of pure zinc for an indefinite period, during which the zinc is oxidated, and forms mammillary concretions on the iron; after which the protective power of the zinc is greatly diminished, and, at this stage, the contact of any substance, even a neutral one,—such as glass,—with the iron, is sufficient to originate oxidation upon it.

"If cast-iron, having a polished surface, is suffered to contract any coating of rust, although the surface be afterwards perfectly polished to the eye, yet zinc, in simple contact, has lost nearly the whole of its power of protection; the zinc and iron both oxidate from the moment of immersion.

* Report of the British Association, Vols. VII. and IX., for 1838 and 1840.

"Of Cast-Iron, in Simple Contact with Zinc, Immersed at an Indefinitely Small Depth in Fresh Water.

"Cast-iron, free from initial rust, so exposed in contact with an equal surface of zinc, is oxidized from the first moment of exposure. The zinc is oxidized from the first, also.

"A plate of iron, whose entire surface was covered with zinc in metallic contact [zinced or galvanized iron], was immersed for twenty-five months in fresh water. On examination, much flocculent zinc had been formed, and lay at the bottom of the glass vessel, which, in some places, was stained with red oxide of iron. The zinc surface was found, in irregularly scattered patches, wholly removed down to the iron, which was covered with peroxide. Hence, about two years appears to be the limit of the preservative power of zinc to iron in fresh water, applied in fusion over its whole surface by the ordinary method. It is to be observed that the zinc surface was removed by solution, unequally or in patches, indicating local action *ab initio;* and it has been shown before that as soon as oxidation takes place at any point upon the iron surface, the protective power of the zinc is diminished at once or rendered null. [The corrosion of both zinc and iron then ensues more rapidly.]

"The conditions the most favorable possible for rapid oxidation of iron consist in its exposure to wet and dry or to air covered with an indefinitely thin film of water, constantly renewed; thus circumstanced, zinc has no protective power over iron in fresh water, and, on the whole, it may be affirmed that, under all circumstances, zinc has not yet been so applied to iron to rank as an electro-chemical protector towards it, in the strict sense."

In a report,* made by Prof. Max Pettenkofer, in reply to the inquiry, how thick a covering of zinc is required to insure permanent protection against the oxidation of iron, the author gives the results of a series of experiments, undertaken by himself, with zinc plate taken from the roof of a building in Munich, where it had been exposed to the atmospheric influences during twenty-seven years. The outer surface was found to be covered with a thick, whitish, oxidized layer, of varying depth, showing that the oxidation had followed the crystalline structure of the metal. By calculation, he determined approximatively, that upon a piece of the zinc, one and a half feet square, there were present 4.264 grammes of zinc rust. By experiment, also, he estimated the amount which had been removed during these twenty-seven years, in the rain-water, in solution and by mechanical displacement, as about 4.117 grammes, making a total of 8.381 grammes.

The preceding observations, which have been made at

* Abhandlungen des naturwissenschaftlich-technischen Commission in München, Vol. I., 1857.

different periods, and were derived from a variety of sources, will be sufficient to illustrate the fact that the zinc of galvanized iron is acted upon by water; that, when allowed to stand in reservoirs or to flow through pipes of this material, water will contain a greater or less amount of zinc, for a longer or shorter period; finally, that, sooner or later, the whole of the zinc will be removed.

With reference to the second part of our first inquiry, —namely, What are the actual products of this action of water upon the zinc?—the conclusions at which we shall be able to arrive will not be so definite. We know that various circumstances, conditions and processes combine to render water, in its ordinary state, a very complex fluid. Receiving its constituents from the air and ground, in various combinations, the laws of which are imperfectly understood, it contains mineral, vegetable and animal matter in suspension, and gaseous, organic and mineral matter in solution. The mode of combination of these various substances in solution cannot be determined, at least with the means at our command at the present day. It is a popular custom, however, for chemists to ascertain, by analysis, the amount of each constituent and then to calculate the probable chemical combinations which have taken place. Carrying out this latter idea, chemists have reported that they have detected the presence of various soluble salts of zinc in water which has been in contact with this metal; the sulphate and the chloride have been reported, principally, and, in some cases, the statement has been made that water has been found "strongly impregnated" with these salts. The real basis of these conclusions is founded upon isolated chemical experiments, made in the laboratory, like the following:—*

"Zinc is rapidly dissolved in a very dilute solution of common salt [chloride of sodium] in water, and may be found in the solution, or water, as the muriate [chloride] of zinc. This would be the action of the common salt in rain-water, and it is the source of the corrosion of zinc roofs."

"Galvanized iron, introduced into a solution of copperas [protosulphate of iron] in water, very dilute, acts thus: I soon found iron-rust rapidly falling on the galvanized pipe. In a short time *all* the iron was precipitated from the water, and fell in a coat of rust, while its place in the water was

* Extract from a report to the City Council of Lowell, Mass. 1842. From Appendix to "Lead Diseases," by L. Tanquerel des Planches, Lowell. 1848.

supplied by zinc. In other words, copperas, or green vitrol, was exchanged for white vitrol."

"Galvanized iron, in a mingled solution of salt and of copperas, such as is found in several wells in Lowell, is rapidly destroyed; the water becomes charged with salts of zinc."

Without entering upon the palpable sources of error in the above experiments, judging them from the published account which is given here, it may be stated that the direct inference implied,—that similar re-actions always take place between zinced iron pipes and water passing through them, and containing the above-mentioned constituents,—is unwarranted.

At the request of the writer, Professor Wm. Ripley Nichols presents the following communication with reference to the action of water upon zinced pipes, and the products of this action :—

MASS. INSTITUTE OF TECHNOLOGY, CHEMICAL LABORATORY,
BOSTON, Dec. 24, 1873.

MY DEAR SIR:—With regard to the action of water on zinc, it is well known that, when zinc is exposed to moist air, it quickly becomes covered with a film of oxide, which soon changes, under the influence of the carbonic acid of the air, into a basic carbonate. The oxide at first formed has been regarded as a *sub-oxide* (Zn_2O), but is now generally held to be the ordinary oxide of zinc (ZnO). That this coating subsequently changes to a basic carbonate, and that the white compound of zinc, which is often found in suspension in water which has been in contact with "galvanized" iron pipes, is a (hydrated) basic carbonate, seems to be sufficiently well established. That the compound is not perfectly definite in its composition, but contains sometimes more, sometimes less, carbonic acid, in proportion to the oxide of zinc, is also an accepted fact.

What, however, is the state in which the zinc exists *dissolved* in water, we do not know, and probably cannot know. Although it has been stated in some cases that a given water contained in solution so much *chloride of zinc*, or so much *sulphate*, such statements rest upon purely gratuitous assumptions.

We have good reason to believe that absolutely pure water would have no action on absolutely pure zinc; but ordinary water contains a quantity, more or less considerable, of different salts, such as chlorides, sulphates, carbonates, and in what form the small amount of zinc in solution exists, it would be impossible to say.

We know that zinc is attacked by a solution of chloride of sodium (common salt), and that a portion goes into solution, hydrogen being at the same time evolved. In the case of a strong solution of chloride of sodium, the amount of zinc that is taken up is so considerable, that it is not unnatural to suppose that a portion of the zinc exists as the double chloride of zinc and sodium; but as undissolved oxide of zinc is also a product of the re-action, and as the solution is found to be alkaline, it is probable that, at the same time, some compound of oxide of zinc and oxide of sodium (zincate of sodium?) is also formed.

In the case of a drinking-water, which is a dilute solution of a variety of salts, the case would be very different, and although we know of this action of chlorides on zinc, we also know that nitrates and sulphates and other salts likewise attack the metal and are capable also of dissolving its oxide; we know further, that the oxide and all the carbonates of zinc dissolve in water containing carbonic acid, so that we are unable to say whether the trace of zinc found in solution existed as chloride, nitrate or sulphate, or as a salt of some organic acid, as (acid?) carbonate, (or carbonate held in solution by carbonic acid), or whether a portion existed in each and all these different states.

I may, perhaps, make my meaning more clear by using an illustration. If we mix together very dilute solutions of chloride of calcium and of sulphate of magnesium, we obtain a mixture which is not distinguishable in appearance from the solutions from which it was produced. If we submit it to chemical examination, we find that it contains a sulphate (or sulphates) and a chloride (or chlorides); also, that it contains magnesium and calcium. Analysis does not, and cannot, show whether the solution contains chloride of calcium and sulphate of magnesium or chloride of magnesium and sulphate of calcium, or whether it contains some chloride and some sulphate of calcium and some chloride and some sulphate of magnesium. The latter view, in fact, has the greater probability; the proportions in which the distribution occurs taking place according to some law at present not understood. But according to the fashion, formerly universal, which even now prevails to a certain extent, the solution, if analyzed, would be said to contain so much sulphate of calcium and so much chloride of magnesium, and for this reason: If the solution be concentrated by evaporation, sulphate of calcium will crystallize out, and may be obtained nearly free from chloride of magnesium. This, however, does not prove the previous existence of all the calcium as sulphate, for the condition of things in the liquid is changed by concentration. It is a general law, that when solutions of two chemical substances are mixed, if such a re-arrangement of the acid and basic radicals is possible, as to form a compound, *insoluble* in the liquid employed, or a *gaseous* compound, such compound will be formed; but where no insoluble or gaseous compound is formed, we cannot judge of the change which takes place.

Therefore, I do not hesitate to say, that we do not, and cannot, know what compound of zinc is present in solution in the case of water which has passed through "galvanized" iron pipes.

Yours respectfully,

WM. RIPLEY NICHOLS.

DR. W. E. BOARDMAN.

Vauquelin and Deyeux,* Devaux and Dejaer,† Mallet,* Schaufele,* Gaultier de Claubry,‡ Tardieu,§ Pettenkofer,* Brande and Taylor,‖ Bouchardat and Fonssagrives,¶ W. R.

* Loc. cit.

† Procès-verbal de la Séance, publ. de la Soc., établie à Liége. 1813.

‡ Annales d'Hygiène et de Medicine légale, t. 42, p. 347. 1849.

§ Dict. d'Hygiène Publique, t. 3, p. 706. 1854.

‖ Chemistry, Am. Ed. 1863.

¶ Journal de Chimie Médicale, t. 10, p. 594. 1864.

Nichols*, all state—indeed, it is a well-known fact—that zinc, when exposed to the action of common, potable water, acquires a coating of oxide, which is practically insoluble in water. This coating, subsequently, is acted upon by the carbonic acid, which comes into contact with it, and it results from this, that the layer is finally composed of oxide, carbonate and a combination of these two, regarded as oxyhydrocarbonate of zinc, by Pettenkofer.† By mechanical and galvanic action and solution, the removal of this layer is effected gradually, and the water then contains more or less of these compounds in suspension, while the remainder enters into solution.

This much, then, is all that can be stated positively, at present, with regard to the nature of the products in question.

In regard to the amount of zinc, in all forms, metallic or other, which may be present in the water, many influences come into consideration. The water may contain ingredients, abnormal in kind or quantity, which will act with unusual energy upon the zinc, or it may be of such purity as to have but a slight action upon the metal. Again, as shown by Mallet,‡ imperfect construction of the material—if the iron be not properly freed from initial rust or if the zinc be incompletely applied, will favor the corrosion of the zinc, for as soon as the iron is exposed, the destruction of the zinc goes on more rapidly. The texture of the zinc, too, whether fine or coarse, affects the results.† If impure zinc be employed, it will be more readily destroyed. The length of time during which pipes have been in use, also, is to be taken into consideration.

The action of potable waters of the purity of the Cochituate is comparatively feeble. We have seen that this water, drawn through pipes which have been in use for eight or nine years, contained only 0.062 grain of metallic zinc to the gallon, while some chemists have reported the presence of from two to six grains§ in the gallon of other waters, and this latter

* See communication in this Report.
† Loc. cit.
‡ Pettenkofer, loc. cit.
§ Boston Med. and Surg. Jour., Jan., 1871, p. 13.

fact is freely admitted by the manufacturers. It is to be observed, however, that in these instances of the presence of such a large amount of zinc, it is always in the form of the carbonate, principally, and the water presents a turbid appearance, which would deter most persons from using it for drinking or in cooking. In the experiments of Schaufèle,* water allowed to stand in galvanized iron vessels for five days, contained only traces of the oxide of zinc.

2. We come now to the consideration of our second inquiry; namely, Do the products, resulting from the action of ordinary drinking-water upon the zinc of galvanized iron, exert a poisonous action upon the human system?

In this inquiry, it seems unnecessary to take into consideration such extraordinary idiosyncrasies as are shown, sometimes, in the inability of individuals to take iron in any form, even in small amounts, or to receive the perfume of a rose without causing asthma. It is not to be denied that a similar extreme susceptibility to some property of zinc, may be the occasion of analogous effects.

It is to be premised, also, that we are not to include in our conclusions, the results which may be due to water unfit for drinking purposes, and which may contain ingredients that would act energetically upon zinc, and contain an unusually large amount of the soluble compounds of this metal.

We have, then, to consider the effects of the oxide, the carbonate and the compounds which occur in solution.

The oxide of zinc, first prepared by Hellot, in 1735, has been employed extensively since his time, both as a medicine and in the arts. Most authorities assert that it is innocuous, while some entertain suspicions of, or attempt to prove its poisonous character.

J. Johnstone,† not including zinc among the mineral poisons, relates, from his own experience, that ten grains of the oxide, taken daily for more than three weeks, were innocuous in the case of a boy about fourteen years of age.

MM. Vauquelin and Deyeux,* on the ground that the oxide, resulting from the action of potable water, is not

* Loc. cit. † Med. Essays and Observations. 1795.

injurious, recommended the use of zinc in the manufacture of reservoirs and water-pipes. This opinion was confirmed by Devaux and Dejaer,* and, a few years later, Orfila,† expressed a similar conviction. MM. Merat and Lens,‡ after enumerating the various uses to which this oxide may be put, remark, "Some writers state that it sometimes gives rise to colic, a phenomenon which we have never observed." They refer, also, to authorities, cited by J. F. Gmelin,§ who ascribe to it an irritant action, "which we believe, is not a fact." Christison‖ makes no reference to any injurious results from the internal use of this oxide, except that he coincides with Orfila, in his estimation of the results obtained by MM. Vauquelin and Deyeux. He also remarks, "that it does not appear that workmen, who are exposed to the fumes of zinc, ever suffer materially." Heller¶ went so far as to state that this oxide might be given up altogether as a medicine, since, being insoluble, it passes through the intestinal canal as inert matter.

M. Blandet** reported cases of supposed poisoning by the fumes of the oxide of zinc. MM. Guerard†† and Levy‡‡ and others, denying the connection of cause and effect in these cases, coincide in the statement that analogous accidents do not ensue from the internal administration of this compound. M. Bouchut,§§ in an elaborate memoir to the French Academy of Sciences, gives an account of the action of oxide of zinc upon the human system. He says, in doses of one to six grammes daily it never occasioned any gastric disturbance; occasionally it gave rise to sleeplessness and restlessness at night. He gives, also, a critical analysis of the classical cases of supposed poisoning by the oxide, which were reported by Blandet in 1844, Bouvier, Landouzy and Maumene in 1850, and shows conclusively that the ill effects in these instances were due to other causes.

In a review of the last-mentioned paper, M. Chevallier‖‖

* Loc. cit.
† Toxicologie Generales. 1818.
‡ Dict. de Matiere Medicale, t. 6. 1834.
§ Apparatus Medicamimum, Vol. I., p. 286. 1795.
‖ Treatise on Poisons, Am. Ed., p. 389. 1845.
¶ Archiv. f. physiol. Heilk. 1847.
** Bulletin de l'Académie. Feb. 17, 1844.
†† Annales d'Hygiene, t. 38, p. 462. 1845.
‡‡ Traite d'Hygiene, etc. 1850.
§§ Annales d'Hygiène, t. 47, p. 5. 1852.
‖‖ Annales d'Hygiène, t. 47, p. 55. 1852.

confirms the opinions of M. Bouchut, and concludes that the oxide of zinc is incapable of producing death, or even of causing any serious effects. He also calls attention to the observations by Michaëlis, of Tubingen,* who stated that he occasioned the death of dogs with daily doses of a few grains of the oxide, a result contrary to those obtained by MM. Flandin,† Orfila‡ and Bouchut.‡ M. Bouchut repeated the experiments upon which Michaëlis founded his opinion, but with negative results.

Pereira§ remarks that this oxide may be taken, in small doses, for a considerable period, without causing any obvious effects: in large doses it sometimes causes temporary giddiness and inebriation. By long-continued use, however, he says, it acts as a slow poison; in proof of which he cites a case‖ where twenty grains were taken daily for about five months. Rapid recovery, however, ensued as soon as the administration of the drug was discontinued. He refers, also, to the cases mentioned above, which were confuted by M. Bouchut and others.

Tardieu‡ states explicitly that zinc imparts no poisonous qualities to water,—a fact which has been proved by theory and confirmed by experience. He refers to facts cited by M. Boutigny,¶ who attributed poisonous qualities to water collected in zinc reservoirs, and remarks that they have not been confirmed and must be regarded as absolutely exceptional, and, without doubt, were due to some special accidental circumstances.

Oesterlen** states that the action of this oxide, when taken internally, is very slight, even in large doses, and expresses his doubts as to the efficacy of the drug, so long accepted, in various diseases. When given to *patients* in large doses, or for a long period, he says, it may give rise to unpleasant symptoms; yet "patients in the Paris hospitals have recently taken one to two ounces daily, and Trousseau†† has given ten

* Archives Générales de Médicine, t. 30. 1852.
† Annales d'Hygiène, t. 47, p. 38. 1852.
‡ Loc. cit.
§ Elements of Mat. Med. and Therapeutics, Vol. I., p. 677. 1852.
‖ British and Foreign Med. Review. July, 1838.
¶ Annales d'Hygiène, t. 17, p. 281.
** Handbuch der Heilmittellehre, p. 165. 1856.
†† See also Report by M. Bouchut, loc. cit.

grains and more, daily, to young children, even without perceiving any deleterious effects."

Schlosberger,* Michaëlis† and others have detected the presence of the metal in several of the secretions of the body. Van Hasselt‡ confirms these facts, and asserts that all compounds of zinc, when introduced into the stomach, are transformed immediately into albuminates, in which form they enter the circulation. He gives his assent to the occasional production of what he terms "zinc dyscrasia," referring to the above cases reported by Pereira. In regard to the cases reported by Blandet (see above), and similar ones by Becquerel, Elfes and Rust, however, he coincides with the more general view, that they were probably due to other causes, which conclusion, he remarks, is all the more probable from the fact that the symptoms disappeared so rapidly on the removal of the supposed cause. The same argument might, with reason, have been applied by himself to the cases which he cites from Pereira in proof of the actual occurrence of "zinc dyscrasia."

Dr. Herpin§ remarks, "The oxide of zinc is perfectly harmless, and may be administered even in doses of six grammes daily, which may be continued for any length of time."

Greenhow‖ mentions a case of what he terms "brass-founders' ague," which, he says, is occasioned by the fumes of deflagrating zinc. These fumes are zinc vaporized in a metallic state and changed into the oxide by contact with the air.¶ This case was similar to those reported by Blandet and others, to which we have already referred, the conclusions in all of which were shown to be erroneous.

Stille,** after citing several reported instances of the ill-effects of this oxide, remarks: "Yet effects of this kind cannot be of ordinary occurrence, for we find that Home†† sometimes gave as much as forty grains a day without injury; that Sieveking cured a case of epilepsy in which thirty-six grains

* Arch. f. physiol. Heilk. 1848.

† Loc. cit.

‡ Allgemeine Giftlehre, übersetz aus dem Holländischen von Dr. J. B. Henkel, p. 322. 1862.

§ Du Prognostic et du Traitement de l'Epilepsie. 1852.

‖ Medical Times and Gazette, Vol. I., p. 227. 1862.

¶ M. Levy, loc. cit.

** Therapeutics and Materia Medica, 2d Ed., Vol. II., p. 138. 1864.

†† Clinical Experiments, p. 220.

of the medicine were taken three times a day, without any unpleasant effect whatever."* He refers, also, to the opinions expressed by Dr. Herpin, and quoted above.

MM. Bouchardat and Fonssagrives,† also, have shown that the oxide which may be contained in drinking-water is innocuous.

Wood and Bache,‡ referring to reported cases of *zinc colic*,§ remark: "This statement, however, is, to say the least, very questionable."

Hirt‖ remarks that some workers in zinc are liable to the ordinary affections to which founders and metal-workers generally are exposed, but that specific effects of zinc (referring to the oxide) have never been proved; that the digestive organs are not affected in the least, a fact upon which he satisfied himself by very extensive observations and inquiries.

Dr. Winsor,¶ of Winchester, Massachusetts, in a recent report, states that it is neither plain, nor is it at all probable, that any person has been in any way poisoned by drinking-water which is impregnated with zinc, in the form of oxide or carbonate. In this opinion, he observes, he is confirmed by inquiry made of skilled analytical chemists, of experts in materia medica and toxicology, manufacturers of zinced pipes, house painters, and others.

The board of water commissioners of Melrose, Massachusetts, in 1871, issued an official circular to "Spot Pond Water Takers in Melrose," in which they urged the immediate removal, or the discontinuance of the use, of galvanized iron service-pipes. The immediate cause of this action on the part of the commissioners seems to have been the occurrence of some cases of sickness, one proving fatal, in the family of the chairman of the board.** The attending medical adviser of the family pronounced them to be cases of zinc poisoning, and J. R. Nichols & Co., of Boston, assent to this opinion, having made an analysis of this water drawn

* On Epilepsy, p. 274.
† Loc. cit.
‡ United States Dispensatory, 12th Ed. 1865.
§ Chemical Gazette, Sept. 16, 1850.
‖ Die Staubinhalations-Krankheiten, p. 99, Breslau. 1871.
¶ Boston Medical and Surgical Journal, Vol. VII., pp. 12 and 238. 1871.
** Boston Journal of Chemistry, Vol. V. 1871.

through and confined around zinced pipes. In this analysis they state the amounts of oxide and carbonate of zinc found in the specimens, and remark: "It is proved by our investigations that the use of galvanized iron service-pipes in conducting Spot Pond water is highly dangerous to health, and should under no circumstance be permitted." An associate of the medical attendant in the above-mentioned cases made a *post mortem* examination in the fatal case, and reported that he found evidences peculiar to zinc poisoning, though he does not state what these appearances were. As no other fatal case is on record, the accuracy of observation, in this instance, may, with good reasons, be questioned. The history of the cases alluded to does not furnish evidence adequate to establish the correctness of the opinion given as to the nature of the illness, in the way of cause and effect.

In another case, communicated by Dr. Bronson, of Attleborough, Massachusetts,* the indefinite symptoms, presented in the report, would point as well to other causes as to mineral poisoning. It seems impossible that in less than two months, —the period in this instance,—symptoms such as described could have been developed by the comparatively small amount of the metal which would be received into the system from the water. Having in mind the variously confirmed facts which are presented in this paper, it must be said of this case, as of the others, that the conclusions are untenable.

From this *résumé* of opinions and facts, it may confidently be asserted, that the oxide of zinc, as it occurs in drinking-water, is absolutely harmless.

With regard to the carbonate of zinc, which is ordinarily found in water drawn through galvanized iron pipes, Vauquelin and Deyeux, Devaux and Dejaer, Orfila and, recently, Bouchardat and Fonssagrives,† were unanimous in their opinion of its innocuity. Eminent chemists, physicians and accepted authorities on materia medica and toxicology in Boston and its vicinity confirm this view. This compound has been administered internally as a medicine for many years, though not very generally, its effects being considered so slight that it has been regarded of little service. Gmelin,

* Boston Med. and Surg. Jour., Vol. VIII., p. 189. 1871.

† See works of these writers already cited.

Merat and Lens and others mention its employment in various affections, but make no reference to any injurious effects resulting from its use. Pereira remarks of its physiological effects, that its action is probably similar to that of the oxide. Oesterlen expresses the same opinion. Van Hasselt remarks, that it does not appear to be so harmless as some writers have asserted, referring to Leclaire, Chevallier and others; but he bases this opinion upon the cases reported by Bouvier, whose deductions, as we have seen, Bouchut showed to be untenable, and upon those communicated by Landouzy and Maumené, which Bouchut, Chevallier, Tardieu and others proved were not occasioned by the action of the carbonate. Dr. T. Stratton, surgeon R. N., who treated two cases of poisoning with the chloride of zinc, states,* that the best antidotes are the carbonated alkalies, which act by converting the poison into the carbonate. Ringer † asserts, that the carbonate being but slightly soluble in the animal fluids, its action on the tissues is very weak, while in large doses it produces some nausea and vomiting; that zinc does not become fixed in the body, nor does it produce chronic affections, like lead or mercury. In fact, the almost universal testimony appears to point conclusively, also, to the innocuity of this compound.

It remains for us to consider the effects of the zinc which is contained in water in a soluble condition. It has been stated in a former part of this paper, that we are unable to say positively what salt or salts of zinc are present in such solutions. In some instances, however, it has been assumed, that the chloride and the sulphate have been present. With equal reason, we might assume, in the case of many drinking-waters, the presence of nearly all the salts of zinc, the acetate, valerianate, iodide, etc. Admitting, then, that water which has been stored in reservoirs or drawn through pipes of galvanized iron always contains zinc in solution, in the form of one or more of its salts, the innocuity of these salts, in the quantities in which they occur, is attested by the experience and experiments of various distinguished observers to whom we have already referred. Vauquelin and Deyeux, Devaux and Dejaer, Orfila, Merat and Lens, Christison, Gaultier de Claubry,

* United States Dispensatory, 12th Ed., p. 1443. 1865.
† Handbook of Therapeutics, 3d Ed., p. 217. 1872.

Chevallier, Tardieu, Bouchardat and Fonssagrives, Winsor, W. R. Nichols and others, while they admit the deleterious influences which may be occasioned by the soluble salts of zinc, when taken internally in sufficient quantity or for a long time, are unanimous in the recommendation of the use of zinced iron for the storing and conveyance of water. This observation naturally suggests the inquiry, what quantity of the different salts, and how long a time, is required for the development of apparent injurious effects? It is impossible, of course, to decide these points absolutely. Approximative conclusions, however, are readily obtainable by reference to the statements and experience of reliable authorities.

Devaux and Dejaer,* in opposition to the conclusions arrived at by Vauquelin and Deyeux,* concluded, from a series of experiments made with Spanish prisoners, that the citrate and acetate of zinc, produced by the action of vegetable acids upon zinc culinary vessels, cannot exert any action upon the human system, in the dose in which they can be found in food and swallowed without being aware of their presence; that in a stronger dose they impart an intolerable flavor, which would constantly cause any aliment to be rejected in which they might chance to be found. Exceptions, however, were taken to the general application of the results of these experiments, by Orfila,* who is sustained by numerous eminent authorities,† on the ground that they were made upon persons of good constitution and in good health, and they were not tried as well with delicate subjects, whose nervous systems were extremely irritable. In the process of cooking, too, other ingredients take part in the energetic action upon these utensils, and in increasing the amount and variety of soluble salts of zinc contained in the food. Most of these authorities, however, assert, at the same time, or imply, that no danger is to be feared from the employment of zinc or zinced material for the storage and conduction of drinking-water.

The sulphate and chloride are known to be the most active poisons of all the salts of zinc; but their harmless character, as they occur in drinking-water, may be shown by reference to experience in their administration as medicines. If this,

* Loc. cit. † See various articles and works cited in previous pages.

then, is true of these salts, it will be apparent that objections to the use of galvanized iron pipes for the conduction of water, on account of the presence of the milder salts, are groundless.

The sulphate has been used for a long time in the practice of medicine. In small doses, from one-half to three or four grains, it has often been administered as a tonic and astringent. But it is observed that the system soon becomes habituated to its use, and in consequence of this fact it is always necessary to increase the dose gradually in order to obtain the desired effects. In this way, very large doses have been given. Babington* gave as much as thirty-six grains, three times a day, without producing any ill effects. Another physician reports† that he has given forty grains, three times a day, for a long period, without any ill effects. Ordinarily, however, it acts as an immediate emetic in large doses. Christison,‡ in regard to the effects of frequent small doses, remarks that he has often given, medicinally, from three to six grains daily, for weeks, without observing any particular effect, except, in some persons, sickness when the larger doses were taken. He adds, others have frequently made the same observation. In fact, it would seem that if the sulphate, which might occur in drinking-water, had any action upon the human system, it would be favorable, in the way of a tonic, rather than otherwise. As an argument, too, in support of the harmless nature of the very small doses which we have under consideration, mention may be made of the very general silence of authorities on the subject.

On the other hand, the acrid, corrosive nature of the chloride of zinc very naturally occasions a suspicion that even small amounts of it would prove injurious. But it has been administered internally, in small doses, for the relief of certain affections, when it has been considered to act as a slight tonic and stimulant. Pereira‡ observes that, taken in very small doses, no obvious effects are produced, except sometimes the amelioration of certain diseases. He states, further, that when applied externally, as a caustic, there is no danger of any constitutional disorder arising from the absorption of the

* Guy's Hosp. Reports, No. 12. 1841.
† Med. Times and Gazette, Vol. I., p. 227. 1862. ‡ Loc. cit.

poison, as is the case with the arsenical and mercurial caustics. Common testimony also establishes the fact that the system becomes habituated to the presence of this compound, so that doses of it require to be increased gradually in chronic affections; in this way, even twelve grains have been given daily without ill effects, though ordinarily one generally commences with a dose of about one-half a grain.

Oesterlen * states that, in small doses, it produces no obvious effects, being similar, in this respect, to the other soluble salts of zinc.

Van Hasselt * observes that the long-continued administration of *two to four* and *more grains* daily is reported to have given rise to affections simulating chronic mercurial poisoning, but makes no mention of ill effects from more minute doses.

Indeed, there seems to be no authority for the assumption that the chloride is injurious, even if it be allowed that the greater part, or the whole, of the zinc, which occurs in solution in water drawn through galvanized iron pipes, is in this form. Further, the fact must be borne in mind that the zinc salt or salts in this water are in an extremely dilute condition,—usually but a small fraction of a grain of metallic zinc being detected in the gallon. Now, it has been estimated † that a healthy adult man consumes a little over four and a half pounds of water daily, in food and drink, or a little less than four and a half pints (apothecaries'). If, then, a given water contained, in solution, one grain of zinc salts to the gallon, which would be absolutely exceptional, only about one-half a grain would enter the stomach in twenty-four hours; and it has been shown that any of these salts may be taken in larger doses, three times daily, with slight, if any, effect upon the system.

Notwithstanding the prejudice existing in a few localities (which we have shown to be unsupported by the facts), against the use of zinced pipes, the general opinion is decidedly opposed to the idea of danger from their employment, and this fact is attested by the constantly increasing demand for such pipes. In Philadelphia alone, where there are five establishments for the manufacture of galvanized iron, about

* Loc. cit.

† Treatise on Human Physiology. By J. C. Dalton, M. D. 3d Ed., p. 70, 1864.

five million feet of pipe were sold during the year 1873 and sent to different parts of the country.

Inquiries addressed to the superintendents of the water works of Salem, Beverly and Cambridge, Massachusetts, and of Portsmouth, New Hampshire, where galvanized iron pipes have been used extensively for several years, have elicited replies, based upon the observation of the writers, the opinions of the water consumers and of reliable physicians and chemists whom they have consulted, to the effect that the use of these pipes is unattended with danger to health. The following extract, from the communication of Mr. D. H. Johnson, Jr., superintendent of the city water works in Salem, will serve to illustrate the general opinion expressed in the above and other communications received by the writer:—

"It is only my province, as a practical man, to give you facts. We have, upon these works, 4,300 services inserted to the walls of buildings, containing 128,500 feet of galvanized iron pipes, or say 24 miles. There are as many more feet of pipes inside the walls of the houses, running (as is generally the case) across the cellars to the back part of the houses, and then up to the draw-faucets in the sinks and to tanks in the top of the buildings. In round numbers, it is safe to say, 48 miles.

"Our medical men in this city have been consulted during the past five years upon the subject, and they have failed to trace, even in a single instance, any disease arising from, or to find any evidence of injurious effects from drinking-water drawn through such pipes."

In the extensive zinc and galvanized iron manufactories of Europe, practical experience and expert testimony* have demonstrated conclusively that the workmen suffer no deleterious effects which could be ascribed to the zinc to which they are exposed in various ways. The same is true of the galvanizing works in this country. In reference to this point, communications have been received from the directors of large establishments in Philadelphia and Pittsburg, Pennsylvania, stating that "the workmen employed are as stout, strong, healthy and able-bodied men as can be found in any of our iron mills," and that none of them have ever been affected with any sickness which was attributed by themselves or physicians to the effects of the zinc to which they

* Consult papers by Bouchet, Chevallier, Levy, Hirt and others, loc. cit.

are constantly exposed. Some of them have been employed in these and in European manufactories for twenty years and more, without having experienced any ill effects, and still do a good day's work.

Many entertain a suspicion that the use of these pipes and tanks may be dangerous, in consequence of the poisonous impurities which, it is said, the zinc coating may contain.

It is known that zinc ore contains many impurities. In the process of smelting, however, it is freed from these to a great extent, though not completely, and commercial zinc or *spelter* is never absolutely pure, but contains, generally, traces of sulphur, iron and arsenic (Brande and Taylor). Other authorities also mention, in addition to the above, lead, tin, cadmium and carbon. In the process of galvanizing iron, again, these impurities become separated from the zinc to a still greater extent, so that the zinc coating contains but the merest trace of them. The essentials of this process have been given before. The zinc is placed in large vats, generally holding about twenty tons, and subjected to a heat of about 740° F. This heat necessarily expels nearly the whole, if not all, of the remaining sulphur and arsenic which were not separated from the original ore by the primary smelting process. At the same time the contained lead, iron, cadmium, etc., are melted with the zinc, but are rapidly deposited at the bottom of the vat, in consequence of their greater specific gravity. These precipitated matters form a waste, called the "dross," which amounts, in each vat, to six or seven thousand pounds weekly, and is shown by analysis to be composed as follows:—

Zinc,	94.88
Iron,	3.55
Tin,	1.00
Lead,	.30
Balance of other metals,	.27
	100.00

The specific gravity of this dross is 7.06, while that of ingot zinc is 6.86. Now, as all iron is zinced from the top

of the vat, it does not come into contact with these impurities, which are at the bottom, and hence the zinc coating can contain but mere traces, if any, of them; at all events not enough to be the occasion of any deleterious effects upon the human system.

Most of the galvanizing in this country is done with the German spelter, which is preferred by manufacturers to the American article, notwithstanding its increased cost, "because it is thought to make the best finish, running brighter and thinner on the iron than the product of our native mines." Now this German zinc contains usually, according to numerous analyses, but a fraction of one per cent. of lead, the only ingredient which can possibly be the occasion of suspicion. As the greater portion of this minute quantity is precipitated to the bottom of the vats, the still more minute quantity which is present in the zinced product, evidently is unworthy of attention in the way of its endangering health.*

To recapitulate: it is proved theoretically, experimentally and practically that zinc is acted upon by ordinary drinking-water; that water, allowed to stand in reservoirs or drawn through pipes of zinced or galvanized iron, usually contains an appreciable amount of zinc, more or less, according to various influences; that the zinc, contained in the water, is in the form of undissolved oxide and carbonate and of dissolved salts, the exact nature of the latter not being known; that probably under no circumstances is the oxide or the carbonate an active or gradual poison, much less in the amounts in which they can occur under the conditions mentioned; that, at least with water fit for drinking purposes in other respects, the contained zinc salts in solution do not exert any deleterious effects upon the human system; finally, that, even if all the zinc in solution were in the form of the chloride, which is known to be the most active poison of the zinc salts, the amount would still be insufficient to endanger health.

* Compare Rep. of State Board of Health of Mass. for 1871, p. 42, as to amounts of lead required to produce injurious effects.